

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 10-298476

(43)Date of publication of application : 10.11.1998

(51)Int.Cl.

C09D 11/02
B41J 2/01

(21)Application number : 09-112089

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(22)Date of filing : 30.04.1997

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(54) RECORDING FLUID FOR INK JET AND ITS PRODUCTION

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a recording fluid which can give a recording of good water resistance even to paper of any kind by mixing a pigment with a water-based resin, an organic colorant derivative, an anthraquinone derivative or an acridone derivative and water.

SOLUTION: The organic colorant derivative, the anthraquinone derivative or the acridone derivative is represented by the formula: Q-[X-N(R1)-Y-R2] (wherein Q is an organic colorant residue, an anthraquinone residue or an acridone residue; X is -SO2-, -CO-, -CH2 or -CH2NHCOCH2-; R1 is H, a 1-18C alkyl or -Y-R2 (wherein R2 is H or a 1-4C alkyl; and Y is moiety of an ethylene oxide polymer or an ethylene oxide/propylene oxide copolymer having an average molecular weight of 400-10,000; and n is 1-3). It is desirable to use a surfactant.

The mixing ratio is such that the pigment, the aqueous resin and e.g. the organic colorant derivative account for 0.5-10 wt.%, based on the total recording fluid, 0.1-10 wt.% and 0.01-20 wt.%, respectively.

LEGAL STATUS

[Date of request for examination] 02.04.2001

[Date of sending the examiner's decision of rejection] 13.07.2004

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's
decision of rejection]

[Date of requesting appeal against examiner's
decision of rejection]

[Date of extinction of right]

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CLAIMS

[Claim(s)]

[Claim 1] The organic-coloring-matter derivative expressed with a pigment, aquosity resin, and the following general formula (1), an anthraquinone derivative or an acridone derivative, and recording ink for ink jets characterized by consisting of water.

General formula (1)

Q-[X-N(R1)-Y-R2] n (however, the inside of a general formula and Q -- organic-coloring-matter residue --) Anthraquinone residue or acridone residue, and X -SO2-, -CO-, -CH2- or -CH2 NHCOCH2-, and R1 The alkyl group or -Y-R2 of H or carbon numbers 1-18, R2 H or the low-grade alkyl group of carbon numbers 1-4, and Y express the ethylene oxide polymer of mean molecular weights 400-10000, or the copolymer section of ethylene oxide and propylene oxide, and n expresses the number of 1-3.

[Claim 2] A pigment, aquosity resin, a surfactant, the organic-coloring-matter derivative expressed with the following general formula (1), an anthraquinone derivative or an acridone derivative, and recording ink for ink jets characterized by consisting of water.

General formula (1)

Q-[X-N(R1)-Y-R2] n (however, the inside of a general formula and Q -- organic-coloring-matter residue --) Anthraquinone residue or acridone residue, and X -SO2-, -CO-, -CH2- or -CH2 NHCOCH2-, and R1 The alkyl group or -Y-R2 of H or carbon numbers 1-18, R2 H or the low-grade alkyl group of carbon numbers 1-4, and Y express the ethylene oxide polymer of mean molecular weights 400-10000, or the copolymer section of ethylene oxide and propylene oxide, and n expresses the number of 1-3.

[Claim 3] Recording ink for ink jets according to claim 1 characterized by including 0.01 - 20 % of the weight for the organic-coloring-matter derivative, anthraquinone derivative, or acridone derivative expressed with 0.5 - 10 % of the weight of pigments, 0.1 - 10 % of the weight of aquosity resin, and a general formula (1) on the basis of the total presentation of ink jet recording ink.

[Claim 4] Recording ink for ink jets according to claim 2 characterized by including 0.01 - 20 % of the weight for the organic-coloring-matter derivative, anthraquinone derivative, or acridone derivative expressed with 0.5 - 10 % of the weight of pigments, 0.1 - 10 % of the weight of aquosity resin, 0 - 10 % of the weight of surfactants, and a general formula (1) on the basis of the total presentation of ink jet recording ink.

[Claim 5] There is no claim 1 which contains an aquosity solvent two to 50% of the weight on the basis of the total presentation of ink jet recording ink, and it is recording ink for ink jets of a publication 4 either.

[Claim 6] There is no claim 1 whose aquosity resin is acrylic copolymer system resin, and it is recording ink for ink jets of a publication 5 either.

[Claim 7] The manufacture approach of claims 1, 3, and 5 and the recording ink for ink jets given in 6 either characterized by diluting to predetermined pigment concentration and filtering with the filter of 1.0 micrometers or less of apertures after carrying out distributed processing of the pigment concentration liquid which is the pigment concentration liquid containing the organic-coloring-matter derivative, anthraquinone derivative, or acridone derivative expressed with a pigment, aquosity resin,

and the above-mentioned general formula (1), and contains a pigment ten to 50% of the weight underwater.

[Claim 8] The manufacture approach of claims 2, 4, and 5 and the recording ink for ink jets given in 6 either characterized by diluting to predetermined pigment concentration and filtering with the filter of 1.0 micrometers or less of apertures after carrying out distributed processing of the pigment concentration liquid which is the pigment concentration liquid containing the organic-coloring-matter derivative, anthraquinone derivative, or acridone derivative expressed with a pigment, aquosity resin, a surfactant, and the above-mentioned general formula (1), and contains a pigment ten to 50% of the weight underwater.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]**[0001]**

[Field of the Invention] This invention distributes a pigment good and relates to the recording ink and its manufacture approach for the ink jets which the record object excelled in the water resisting property.

[0002]

[Description of the Prior Art] As recording ink for ink jets, what dissolved water soluble dye, such as acid dye, direct dye, and basic dye, in a glycol system solvent and water is used well conventionally (for example, JP,53-61412,A, JP,54-89811,A, JP,55-65269,A, etc.). As water soluble dye, in order to acquire the stability of recording ink, generally the soluble high thing to water is used. Therefore, the ink jet record object had the problem of producing a blot of the color of a record part easily, when the water resisting property was bad and generally spilt water.

[0003] In order to improve such a waterproof defect, the structure of a color is changed or to prepare strong basic recording ink is tried (for example, JP,56-57862,A etc.). Moreover, aiming at waterproof improvement, using the reaction of the recording paper and recording ink well is also performed (for example, JP,50-49004,A, JP,57-36692,A, JP,59-20696,A, JP,59-146889,A, etc.). Although these approaches are obtaining effectiveness remarkable about a certain kind of detail paper, since various detail paper is used for them in record by the ink jet method, in the recording ink which uses water soluble dye, sufficient water resisting property of a record object is not obtained in many cases.

[0004] Moreover, although there are what distributed thru/or dissolved the oil color in the high boiler, and a thing which dissolved the oil color in the volatile solvent as waterproof good recording ink, depending on the installation of the case where it may be disliked on an environment to the odor of a solvent, or discharge of a solvent, and a lot of record is performed, or equipment, needs, such as solvent recovery, may pose a problem. Therefore, in order to receive the water resisting property of a record object, development of the recording ink which distributed the pigment to the drainage system medium is performed. However, in order to acquire the distributed stability of a pigment, detailed-ization of enough pigments is needed and selection of the compound which makes stability distribute a pigment is needed in this manufacture.

[0005]

[Problem(s) to be Solved by the Invention] The purpose of this invention is in offer of the recording ink for moisture powder ink jets with which a waterproof good record object is obtained to any papers, and its easy manufacture approach.

[0006]

[Means for Solving the Problem] That is, the 1st invention relates to the organic-coloring-matter derivative expressed with a pigment, aquosity resin, and the following general formula (1), an anthraquinone derivative or an acridone derivative, and the recording ink for ink jets characterized by consisting of water.

General formula (1)

Q-[X-N(R1)-Y-R2]ⁿ (however, the inside of a general formula and Q -- organic-coloring-matter residue

--) Anthraquinone residue or acridone residue, and X -SO2-, -CO-, -CH2- or -CH2 NHCOCH2-, and R1 The alkyl group or -Y-R2 of H or carbon numbers 1-18, R2 H or the low-grade alkyl group of carbon numbers 1-4, and Y express the ethylene oxide polymer of mean molecular weights 400-10000, or the copolymer section of ethylene oxide and propylene oxide, and n expresses the number of 1-3.

[0007] The 2nd invention is a pigment, aquosity resin, a surfactant, the organic-coloring-matter derivative expressed with the following general formula (1), an anthraquinone derivative or an acridone derivative, and recording ink for ink jets characterized by consisting of water.

General formula (1)

Q-[X-N(R1)-Y-R2] n (however, the inside of a general formula and Q -- organic-coloring-matter residue

--) Anthraquinone residue or acridone residue, and X -SO2-, -CO-, -CH2- or -CH2 NHCOCH2-, and R1 The alkyl group or -Y-R2 of H or carbon numbers 1-18, R2 H or the low-grade alkyl group of carbon numbers 1-4, and Y express the ethylene oxide polymer of mean molecular weights 400-10000, or the copolymer section of ethylene oxide and propylene oxide, and n expresses the number of 1-3.

[0008] The 3rd invention is recording ink for ink jets 1st given in invention characterized by including 0.01 - 20 % of the weight for the organic-coloring-matter derivative, anthraquinone derivative, or acridone derivative expressed with 0.5 - 10 % of the weight of pigments, 0.1 - 10 % of the weight of aquosity resin, and a general formula (1) on the basis of the total presentation of ink jet recording ink.

[0009] The 4th invention is recording ink for ink jets 2nd given in invention characterized by including 0.01 - 20 % of the weight for the organic-coloring-matter derivative, anthraquinone derivative, or acridone derivative expressed with 0.5 - 10 % of the weight of pigments, 0.1 - 10 % of the weight of aquosity resin, 0 - 10 % of the weight of surfactants, and a general formula (1) on the basis of the total presentation of ink jet recording ink.

[0010] the 1st invention in which the 5th invention contains an aquosity solvent two to 50% of the weight on the basis of the total presentation of ink jet recording ink thru/or the 4th invention -- it is recording ink for ink jets of a publication either.

[0011] the 1st invention whose aquosity resin of the 6th invention is acrylic copolymer system resin thru/or the 5th invention -- it is recording ink for ink jets of a publication either.

[0012] The organic-coloring-matter derivative by which the 7th invention is expressed with a pigment, aquosity resin, and the above-mentioned general formula (1), It is the pigment concentration liquid containing an anthraquinone derivative or an acridone derivative. invention of the 1st, 3, 5, and 6 characterized by diluting to predetermined pigment concentration and filtering with the filter of 1.0 micrometers or less of apertures after carrying out distributed processing of the pigment concentration liquid which contains a pigment ten to 50% of the weight underwater -- it is the manufacture approach of the recording ink for ink jets a publication either.

[0013] The organic-coloring-matter derivative by which the 8th invention is expressed with a pigment, aquosity resin, a surfactant, and the above-mentioned general formula (1), It is the pigment concentration liquid containing an anthraquinone derivative or an acridone derivative. invention of the 2nd, 4, 5, and 6 characterized by diluting to predetermined pigment concentration and filtering with the filter of 1.0 micrometers or less of apertures after carrying out distributed processing of the pigment concentration liquid which contains a pigment ten to 50% of the weight underwater -- it is the manufacture approach of the recording ink for ink jets a publication either.

[0014]

[Embodiment of the Invention] Hereafter, this invention is explained to a detail. As a pigment of this invention, the various organic pigments and inorganic pigment which are used for printing ink, a coating, etc. are usable. As an organic pigment, for example, a phthalocyanine pigment, insoluble azo pigment, An azo lake pigment, a bends imidazolone system pigment, an anthraquinone pigment, A quinacridone pigment, a dioxazine pigment, a diketo pyrrolo pyrrole pigment, An anthra pyrimidine pigment, an anthanthrone pigment, an indan SURON pigment, A flavan SURON pigment, a peri non pigment, a perylene pigment, an isoindolinone pigment, a thioindigo pigment, etc. can be mentioned. As an inorganic pigment Carbon black, ferrous oxide, the white lead, a minium, ultramarine blue, Berlin blue, cobalt oxide, A titanium dioxide, a titanium-dioxide covering mica, strontium chromate, Titanium

yellow, black titanium oxide, Zinc chromate, iron black, molybdate red, a molybdenum white, a lithopone, emerald green, cadmium yellow, cadmium red, cobalt blue, etc. can be mentioned. What could be used in the state of the aquosity slurry after pigment generation and the wet cake, and carried out disintegration of this slurry by desiccation of spray dry etc. is sufficient as such a pigment.

[0015] However, what made particle diameter detailed in manufacture of recording ink since the flight stability as recording ink had the good one where the particle diameter of a pigment is smaller is desirable. Or it is desirable to choose the pigment which can carry out [detailed]-izing at the process of distribution. As particle diameter of a desirable pigment, 0.2 micrometers or less are 0.1 micrometers or less still more preferably in the mean particle diameter by the centrifuge. Filtration actuation of an in [that it is such a particle size / manufacture of recording ink] is easy, and sedimentation's in storage of recording ink decreases. The loadings of a pigment blend 2 - 4 % of the weight preferably 0.5 to 10% of the weight on the basis of the total presentation of the recording ink for ink jets.

[0016] The organic-coloring-matter derivative in this invention, an anthraquinone derivative, or an acridone derivative is expressed with a general formula (1).

General formula (1)

Q-[X-N(R1)-Y-R2] n (however, the inside of a general formula and Q -- organic-coloring-matter residue --) Anthraquinone residue or acridone residue, and X -SO2-, -CO-, -CH2- or -CH2 NHCOCH2-, and R1 The alkyl group or -Y-R2 of H or carbon numbers 1-18, R2 H or the low-grade alkyl group of carbon numbers 1-4, and Y express the ethylene oxide polymer of mean molecular weights 400-10000, or the copolymer section of ethylene oxide and propylene oxide, and n expresses the number of 1-3.

[0017] As organic-coloring-matter residue in a general formula (1), anthraquinone system coloring matter, acridone system coloring matter, azo dye, phthalocyanine system coloring matter, Quinacridone system coloring matter, dioxazine system coloring matter, anthra pyrimidine system coloring matter, anthanthrone system coloring matter, indan SURON system coloring matter, flavan SURON system coloring matter, pyran SURON system coloring matter, peri non system coloring matter, perylene system coloring matter, a thioindigo system, etc. are mentioned.

[0018] In addition, anthraquinone or acridone presents a "color", when it has the so-called auxochromes, such as -CH3, -OH, -OR, -NH2, -NHR, -NR2, -Cl, and -Br. Therefore, in this invention, the anthraquinone residue as Q in a general formula (1) and acridone residue are the anthraquinone and acridones which do not have the above auxochromes, and the anthraquinone system coloring matter as organic-coloring-matter residue and acridone system coloring matter are the anthraquinone and acridones which have the above-mentioned auxochrome among Q.

[0019] X is -SO2-, -CO-, -CH2-, or -CH2 NHCOCH2-. Y is the ethylene oxide polymer of mean molecular weights 400-10000, or the copolymer section of ethylene oxide and propylene oxide.

Although the ratio of ethylene oxide and propylene oxide is arbitrary, 50% or more of thing has the desirable ratio of ethylene oxide in respect of the effectiveness in distribution.

[0020] The manufacture approach of the organic-coloring-matter derivative of the general formula (1) in this invention, an anthraquinone derivative, and an acridone derivative With a conventional method, to organic coloring matter, anthraquinone, or acridone -SO2 Cl, - Introduce substituents, such as COCl, - CH2 Cl, and -CH2 NHCOCH2 Cl. The method of making it react with monochrome or a screw-(polyoxyalkylene) amine under alkali catalyst existence in reaction solvents, such as water, alcohol, acetone or N, and N'-dimethylformamide, depending on the case, and removing a solvent is common. Moreover, it is industrially more advantageous to carry out coupling, after making monochrome or a screw-(polyoxyalkylene) amine react to a diazo component or a coupler component beforehand in the case of an azo pigment.

[0021] this invention -- setting -- the organic-coloring-matter derivative, anthraquinone derivative, or acridone derivative (henceforth the organic-coloring-matter derivative of a general formula (1) etc.) of a general formula (1) -- an inn -- a lot -- the pigment-content powder of jet recording ink -- more -- detailed-izing -- it stabilizes and regurgitation stability from a nozzle and preservation stability are made good. As for the loadings of the organic-coloring-matter derivative of the general formula (1) in this invention etc., it is desirable to blend 0.01 - 20 % of the weight on the basis of the total presentation of

the recording ink for ink jets. Effectiveness is not looked at by detailed-izing of the pigment-content powder which will be obtained if fewer than 0.01 % of the weight, and stabilization, but the filterability at the time of the recording ink manufacture for ink jet worsens, or the nozzle blinding by the floc in the case of printing and the regurgitation stability by the increment in viscosity worsen. Moreover, if it uses more mostly than 20 % of the weight, the quality of other ink jet recording ink will be influenced, and the permeability to paper, a water resisting property, etc. will worsen.

[0022] It is more advantageous to select the thing of the chemical structure which has a frame that an organic-coloring-matter derivative is the same as that of the pigment to be used among the organic-coloring-matter derivatives of the general formula (1) of this invention etc. or similar. That is, as compared with a case effectiveness being not only large but pigment independent, change of a hue is desirable few to cohesionless, amorphism, a fluidity, etc. Moreover, the anthraquinone derivative obtained from anthraquinone residue among the organic-coloring-matter derivatives of a general formula (1) etc. and the acridone derivative obtained from acridone residue are like [which are coloring colorlessness or slightly], and even if it adds to various pigments, there is little change of a hue and it is advantageous at the point of excelling in versatility.

[0023] As for the organic-coloring-matter derivative expressed with a general formula (1) in this invention, it is common to add and to use at the time of distribution of a pigment. Moreover, it can be used mixing with a pigment beforehand and can also carry out. For example, after making a pigment suspend in water or an organic solvent, mixing the organic-coloring-matter derivative of a general formula (1) etc. and making it stick to a pigment front face, it is an approach using the pigment constituent obtained by removing water or an organic solvent. Moreover, it can also be used by mixing the organic-coloring-matter derivative expressed with a general formula (1) in a pigment chemically-modified degree. It is an approach using the pigment constituent obtained in an azo pigment in detail by mixing the organic-coloring-matter derivative of a general formula (1) etc., and drying during coupling if needed after filtration in a phthalocyanine pigment, a quinacridone pigment, a dioxazine pigment, etc. in pigment chemically-modified degrees, such as the salt milling method and a sulfuric-acid solution process.

[0024] Since fixing to the stability of distribution of a pigment and the printing hand-ed of recording ink is made good, the aquosity resin used in this invention can be used. As aquosity resin, there is independent [no], it can mix and the resin of dispersibility can be used for the resin and water of dissolved water in fuel which dissolve in water. As such resin, the resin of dispersibility is mentioned to the resin and water of dissolved water in fuel which dissolve in water, such as an acrylic copolymer system, a polyester system, a polyamide system, and a polyurethane system. If needed, neutralizers, such as ammonium, an amine, and inorganic alkali, can be adjusted suitably, and these resin can add them.

[0025] The weight average molecular weight 5000-300000 and the acid number which are obtained by acrylic copolymer system resin carrying out the solution polymerization of 5 - 30 % of the weight of carboxylic-acid content monomers, such as 50 - 80 % of the weight of acrylic-acid (meta) alkyl ester, an acrylic acid, a methacrylic acid, a maleic acid, and an itaconic acid, and the 0 - 20 % of the weight of the other monomers in an emulsion polymerization or a water-soluble solvent are resin of 1-200. As the above-mentioned (meta) acrylic-acid alkyl ester, there are a methyl acrylate (meta), an ethyl acrylate (meta), acrylic-acid (meta) propyl, acrylic-acid (meta) n-butyl, acrylic-acid (meta) isopropyl, isobutyl acrylate (meta), 2-ethylhexyl acrylate (meta), acrylic-acid (meta) n-hexyl, acrylic-acid (meta) lauryl, etc. As the above and other monomers, there are acrylic-acid (meta) 2-hydroxyethyl, 2-hydroxypropyl acrylate (meta), acrylamide, N-methylol acrylamide, diacetone acrylamide, glycidyl (meta) acrylate, styrene, vinyltoluene, vinyl acetate, acrylonitrile, vinyl alcohol, ethylene, etc. Aquosity resin blends 0.5 - 3 % of the weight preferably 0.1 to 10% of the weight on the basis of the total presentation of the recording ink for ink jets.

[0026] In this invention, anionic, nonionic, cationicity, and both the ionicity activator can be used as a surface active agent if needed. As an anionic activator, a fatty-acid salt, an alkyl-sulfuric-acid ester salt, alkylaryl sulfonates, Alkylnaphthalenesulfonate, a dialkyl sulfonate, dialkyl sulfo succinate, Alkyl diaryl ether disulfon acid chloride, alkyl phosphate, a polyoxyethylene-alkyl-ether sulfate, A polyoxyethylene-

alkyl-aryl-ether sulfate, a naphthalene sulfonic-acid formalin condensate, polyoxyethylene alkyl phosphate, glycerol borate fatty acid ester, polyoxyethylene glycerol fatty acid ester, etc. can be illustrated. As a nonionic activator, nonionic activators, such as polyoxyethylene alkyl ether, polyoxyethylene alkyl aryl ether, a polyoxyethylene oxypropylene block copolymer, a sorbitan fatty acid ester, polyoxyethylene sorbitan fatty acid ester, polyoxyethylene sorbitol fatty acid ester, a glycerine fatty acid ester, polyoxyethylene fatty acid ester, polyoxyethylene alkylamine, a fluorine system, and a silicon system, can be illustrated. As a cationic activator, an alkylamine salt, quaternary ammonium salt, alkyl pyridinium salt, an alkyl imidazolium salt, etc. can be illustrated. As both ionicity activator, an alkyl betaine, an alkylamine oxide, phosphaJIRUKORIN, etc. can be illustrated. By using with the organic-coloring-matter derivative expressed with a general formula (1), a surfactant promotes detailed-ization of the pigment particle in distribution, and the preservation stability of recording ink increases it. A surface active agent blends 0.5 - 3 % of the weight preferably 0.1 to 10% of the weight on the basis of the total presentation of the recording ink for ink jets.

[0027] Although the ink jet recording ink of this invention can be manufactured by various approaches, it is desirable to blend with the dispersion liquid of aquosity resin, a solution, or the solution of a surfactant the pigment concentration liquid (b) containing the organic-coloring-matter derivative expressed with the pigment concentration liquid (a) containing the organic-coloring-matter derivative expressed with a pigment, aquosity resin, and a general formula (1) or a pigment, aquosity resin, a surfactant, and a general formula (1), and to dilute to predetermined pigment concentration. It is desirable still more desirable that it is 10 - 50 % of the weight, and pigment concentration liquid (a) or the pigment concentration in (b) is 10 - 30 % of the weight. Moreover, as for pigment concentration liquid (a) or the aquosity resin in (b), and a surfactant, it is desirable that it is 2.5 - 20 % of the weight, respectively. Furthermore, it is more desirable for the ratio of the total quantity of the organic-coloring-matter derivative expressed with a pigment and a general formula (1) in pigment concentration liquid (a) or (b) and the total quantity of aquosity resin and a surfactant to be 6/4 or more.

[0028] As a disperser for obtaining the pigment concentration liquid (a) to apply or (b), a dissolver, a high speed mixer, a homomixer, a paint shaker, a ball mill, attritor, a sand mill, a jet mill, micro sieve TAIZA, etc. are mentioned. Moreover, a pigment, the pigment agent of a general formula (1) and aquosity resin, or a surfactant can also be beforehand kneaded well in a kneader and 2 roll mills as pretreatment distributed by the above-mentioned disperser. In this way, the obtained pigment concentration liquid (a) or (b) can be suitably diluted with water, aquosity resin, etc., and ink jet recording ink can be manufactured by mixing a required additive.

[0029] The recording ink of this invention may blend an aquosity solvent, a penetrating agent, antiseptics, etc. other than a pigment, water, a pigment agent, aquosity resin, and a surfactant, and can add coloring adjuvants, such as a color, a chelating agent, PH regulator, a defoaming agent, etc. if needed further. As an aquosity solvent, desiccation in the nozzle part of recording ink and solidification of recording ink are prevented, and injection of stable **** recording ink and desiccation by the passage of time of a nozzle are prevented. As such an aquosity solvent, ethylene glycol, a diethylene glycol, Propylene glycol, triethylene glycol, a polyethylene glycol, GURISERINN, tetraethylene glycol, dipropylene glycol, The ketone alcohol, ethylene glycol monobutyl ether, ethylene-glycol-monobutyl-ether ethylene glycol monoethyl ether, 1, 2-hexandiol, a N-methyl-2-pyrrolidone, a permutation pyrrolidone, 2 and 4, 6-hexane triol, tetra-furfuryl alcohol, 4-methoxy-4 methyl pentanone, etc. can be mentioned. Moreover, alcohols, such as a methanol, ethanol, and isopropyl alcohol, can also be used in the purpose which speeds up desiccation in the paper of recording ink. There is independent [no], it mixes and these aquosity solvents are used in 2 - 50% of the weight of the range on the basis of the total presentation of ink jet recording ink. The ion exchange water thru/or distilled water from which the metal ion etc. was removed is used for the water which is the medium of recording ink. A urea, a dimethyl urea, etc. can also be added as other additives.

[0030] At the time [like paper] whose printing hand-ed of recording ink is, since osmosis of the recording ink to paper is sped up and it makes drying [apparent] quick, a penetrating agent can be added. As such a penetrating agent, the glycol ether [, such as the diethylene-glycol monobutyl ether

described as an aquosity solvent,], alkylene glycol, and polyethylene-glycol mono-lauryl ether, sodium lauryl sulfate, sodium dodecylbenzenesulfonate, sodium oleate, sodium dioctyl sulfosuccinate, etc. can be used. if [than this] more [these have effectiveness sufficient by the amount of 5 or less % of the weight used of recording ink and] -- a blot of printing and a paper omission (print through) -- a lifting -- it is not desirable. Antiseptics prevent putrefaction of recording ink and generating of mold, and the amine salt of sodium dehydroacetate, a sodium benzoate, sodium pyridine thione-1-oxide, zinc pyridine thione-1-oxide, 1, 2-bends iso thiazoline-3-ON, and 1-bends iso thiazoline-3-ON etc. is used. These have the desirable thing of recording ink used about 0.05 to 1.0% of the weight.

[0031] As a color, it can be used in a form which does not have a problem in a water resisting property and lightfastness for the purpose of adjustment of the hue of a pigment, grant of concentration, etc. Since stability of distribution of a pigment may be worsened by use of a color, it is necessary to stop this better ** to 25 or less % of the weight of use 40 or less % of the weight of a pigment. As a color, acid dye, basic dye, direct dye, reactive dye, a disperse dye, metallized dye, etc. are raised. These colors have the desirable purification color from which mineral salt was removed. As for a chelating agent, it is desirable to block the metal ion in recording ink, to prevent a deposit of an insolubility object etc. in a deposit of the metal in the nozzle section or recording ink, and to use the sodium salt of ethylenediamine TETORAASE tick acid and ethylenediamine TETORAASE tick acid, the diammonium salt of ethylenediamine TETORAASE tick acid, the tetra-ammonium salt of ethylenediamine TETORAASE tick acid, etc. 0.005 to 0.5% of the weight. Moreover, since it adjusts to PH of a request of PH of recording ink and stability with the stability of recording ink thru/or recording ink piping in a recording device is acquired, the buffer solutions, such as regulators, such as an amine, mineral salt, and ammonia, and a phosphoric acid, can be used. Moreover, since generating of the bubble at the time of circulation of recording ink or migration, and manufacture of recording ink is prevented, a defoaming agent can also be added.

[0032] As for the mixed recording ink, it is desirable to filter with the filter of 1.0 micrometers or less of apertures in front of dilution or in the back, and it is still more desirable to filter with a filter 0.45 micrometers or less. In advance of filtration of a filter, according to centrifugal separation, a beforehand big particle is also separable, blinding in filtration with a filter can be lessened by this, and the frequency of filter exchange can be lessened. Recording ink is adjusted as a liquid with a viscosity of 0.8-15cps (25 degrees C), although based also on the method of a recording device. Surface tension is 25 - 60 dyn/cm. Although especially PH is not restrained, the range of it is 4-12, and this better ** has the desirable alkalescence of 7-9.

[0033] Though it is aquosity, since the recording ink manufactured by this invention has the remarkably good water resisting property, suitably use [recording ink / as recording ink for ink jets], it can begin to draw up the document in office, and it can use it in fields, such as address writing of mail, marking of corrugated paper, numbering, and a bar code. Moreover, compared with the recording ink manufactured by the color, lightfastness is also good, and a dominance shelf life [of a record object] color picture can be formed.

[0034]

[Example] Hereafter, this invention is explained based on an example. The "weight section" is expressed as the "section" among an example, and "% of the weight" is expressed as "%", respectively.

[0035] The example of manufacture 1 chloromethyl copper-phthalocyanine 150 section, N, and N-screw-(polyoxyethylene) amine (however, number of average polymerization mols of ethyleneoxide 15 mols) 349 section and the methanol 2000 section are mixed, and it holds at 65 degrees C for 4 hours. Subsequently, reduced pressure distilling off of filtration and the methanol was carried out, and the paste containing the (Compound a) 504 section was obtained.

[0036] The example of manufacture 2 copper-phthalocyanine sulfonyl chloride (an average of 1.5 chloro sulfonyl groups per molecule are contained.) 143 section, the N-polyoxyalkylene amine (however, number of average polymerization mols ten mol [of propylene oxide], 32 mols of ethyleneoxides) 600 section, the pyridine 160 section, and the methanol 2000 section are mixed, and it holds at 65 degrees C for 4 hours. Subsequently, reduced pressure distilling off of filtration and the solvent was carried out,

and the paste containing the (Compound b) 450 section was obtained.

[0037] The example of manufacture 3 copper-phthalocyanine sulfonyl chloride (an average of two chloro sulfonyl groups per molecule are contained.) 150 section, the N-polyoxyalkylene amine (however, number of average polymerization mols three mol [of propylene oxide], 19 mols of ethyleneoxides) 240 section, and the isopropyl alcohol 2000 section are mixed, and it holds at 65 degrees C for 4 hours. Subsequently, reduced pressure distilling off of filtration and the isopropanal pull alcohol was carried out, and the paste containing the (Compound c) 310 section was obtained.

[0038] The example of manufacture 4 chloroacetic-acid amide methyl copper-phthalocyanine (an average of 1.7 chloroacetic-acid amide methyl groups per molecule are contained.) 150 section, the N-polyoxyalkylene amine (however, number of average polymerization mols three mol [of propylene oxide], 19 mols of ethyleneoxides) 240 section, and the isopropyl alcohol 2000 section are mixed, and it holds at 65 degrees C for 4 hours. Subsequently, reduced pressure distilling off of filtration and the isopropanal pull alcohol was carried out, and the paste containing the (Compound d) 310 section was obtained.

[0039] Coupling of the 4 and 4-dichlorobenzidine was carried out to the suspension of the 5N-polyoxyalkylene-4 of examples of manufacture-aceto acetyl amino benzenesulphonyl amide (however, number of average polymerization mols ten mol [of propylene oxide], 32 mols of ethyleneoxides) 300 section, and the water 1000 section with the conventional method, and filtration and the paste which carries out reduced pressure distilling off of the solvent, and contains the (Compound e) 320 section were obtained.

[0040] After changing the copper-phthalocyanine sulfonyl chloride 143 section of the example 2 of example of manufacture 6 manufacture into the Quinacridone sulfonyl chloride (an average of 1.5 chloro sulfonyl groups per molecule are contained.) 96.0 section and compounding it, the unreacted object and the solvent were removed and the paste containing the (Compound f) 191 section was obtained.

[0041] After changing the copper-phthalocyanine sulfonyl chloride 143 section of the example 2 of example of manufacture 7 manufacture into the dioxazine sulfonyl chloride (an average of 1.7 chloro sulfonyl groups per molecule are contained.) 157 section and compounding it, the unreacted object and the solvent were removed and the paste containing the (Compound g) 575 section was obtained.

[0042] The example of manufacture 8 anthraquinone-2-carbonyl chloride 82 section, the N-polyoxyalkylene amine (however, number of average polymerization mols ten mol [of propylene oxide], 32 mols of ethyleneoxides) 600 section, the pyridine 160 section, and the acetone 2000 section are mixed, and it holds at 55 degrees C for 4 hours. Subsequently, reduced pressure distilling off of filtration and the solvent was carried out, and the paste containing the (Compound h) 400 section was obtained.

[0043] Compound (i) - (n) shown in Table 1 according to the example 9 of manufacture - the examples 1-8 of 14 manufactures was compounded. In addition, in the column of the substituent of a front Naka organic-coloring-matter derivative, an anthraquinone derivative, or an acridone derivative, -15EO- shows that the average degree of polymerization of ethyleneoxide is 15, and, in -10PO/32EO-, the average degree of polymerization of propylene oxide shows that the average degree of polymerization of 10 and ethyleneoxide is 32.

[0044]

[Table 1]

製造例	一般式(1) の化合物 の記号	構造および組成		
		有機色素残基等の名称	置換基	置換基数
1	(a)	C. I. Pigment Blue 15	-CH ₂ N(15EO-H) ₂	1
2	(b)	C. I. Pigment Blue 15	-SO ₂ NH-10PO/32EO-Me	1. 5
3	(c)	C. I. Pigment Blue 15	-SO ₂ NH-3PO/19EO-Me	2
4	(d)	C. I. Pigment Blue 15	-CH ₂ NHCOCH ₂ NH-3PO/19EO-Me	1. 7
5	(e)	C. I. Pigment Yellow 83	-SO ₂ NH-10PO/32EO-Me	1
6	(f)	C. I. Pigment Violet 19	-SO ₂ NH-10PO/32EO-Me	1. 5
7	(g)	C. I. Pigment Violet 23	-SO ₂ NH-10PO/32EO-Me	1. 7
8	(h)	アントラキノン	-CONH-10PO/32EO-Me	1
9	(i)	C. I. Pigment Blue 15	-SO ₂ NH-32PO/3EO-Me	2
10	(j)	C. I. Pigment Yellow 17	-SO ₂ NH(15EO-H) ₂	1
11	(k)	C. I. Pigment Yellow 108	-SO ₂ NH-3PO/19EO-Me	1
12	(l)	C. I. Pigment Yellow 151	-SO ₂ NH-10PO/32EO-Me	1
13	(m)	C. I. Pigment Violet 19	-CH ₂ NHCOCH ₂ NH-10PO/32EO-Me	1. 7
14	(n)	アクリドン	-CONH-10PO/32EO-Me	1

[0045] [Example 1] The following raw material was mixed, it distributed for 12 hours using the paint shaker, and the concentration liquid of moisture powder ink jet recording ink was produced.

RIONORU blue FG-7300 (pigment: TOYO INK MFG. CO., LTD. make) The 19.0 sections JON krill 61J The 16.4 sections (31.0% Johnson polymer company make of styrene acrylic copolymer solid content)

Emulgen A-90 (surfactant) The 5.0 sections Compound (a) The 4.8 sections Ion exchange water By 58.6 ******, the above-mentioned concentration liquid and the following were mixed and the diethylene-glycol monobutyl ether was adjusted to suitableness in addition the viscosity of 2.5cps (25 degrees C), and surface tension 40 dyn/cm. Behind, 1.0-micrometer membrane filter was used and filtered, it filtered using 0.45 more micrometer membrane filter, and moisture powder ink jet recording ink was produced.

The above-mentioned concentration liquid The 12.5 sections Emma Polly TYN-40 The 5.5 sections (made in 44.8% Gifu shellac factory of styrene acrylic copolymer solid content)

Glycerol The 10.0 sections Ion exchange water The 72.0 sections [0046] [Examples 2-4] According to the example 1, moisture powder ink jet recording ink was produced using a compound (b), (h), and (i).

[0047] [Example 5] The following raw material was mixed, it distributed for 12 hours using the paint shaker, and the concentration liquid of moisture powder ink jet recording ink was produced.

RIONORU blue FG-7300 (pigment: TOYO INK MFG. CO., LTD. make) The 19.0 sections JON krill 61J The 16.4 sections (31.0% Johnson polymer company make of styrene acrylic copolymer solid content)

Compound (c) The 9.8 sections Ion exchange water By 58.6 ******, the above-mentioned concentration liquid and the following were mixed and the diethylene-glycol monobutyl ether was adjusted to suitableness in addition the viscosity of 2.5cps (25 degrees C); and surface tension 40 dyn/cm. Behind, 1.0-micrometer membrane filter was used and filtered, it filtered using 0.45 more micrometer membrane filter, and moisture powder ink jet recording ink was produced.

The above-mentioned concentration liquid The 12.5 sections Emma Polly TYN-40 The 5.5 sections (made in 44.8% Gifu shellac factory of styrene acrylic copolymer solid content)
Glycerol The 10.0 sections Ion exchange water The 72.0 sections [0048] [Example 6] According to the example 5, moisture powder ink jet recording ink was produced using the compound (d).
[0049] [Example 7] The following raw material was mixed, it distributed for 24 hours using the paint shaker, and the concentration liquid of moisture powder ink jet recording ink was produced.
HOSUTA palm Pink E (pigment Hoechst A.G. make) The 19.4 sections JON krill 62 The 14.7 sections (34.0% Johnson polymer company make of styrene acrylic copolymer solid content)
Emulgen A-90 The 2.4 sections Compound (f) The 5.0 sections Ion exchange water The above-mentioned concentration liquid and the following were mixed by 60.3 ******, and the diethylene-glycol monobutyl ether was adjusted to suitableness in addition the viscosity of 2.5cps (25 degrees C), and surface tension 40 dyn/cm. Behind, 1.0-micrometer membrane filter was used and filtered, it filtered using 0.45 more micrometer membrane filter, and moisture powder ink jet recording ink was produced.
The above-mentioned concentration liquid The 12.5 sections Emma Polly TYN-40 The 5.5 sections Glycerol The 10.0 sections Ion exchange water The 72.0 sections [0050] [Example 8] According to the example 7, moisture powder ink jet recording ink was produced using Compound m.
[0051] [Example 9] The following raw material was mixed, it distributed for 24 hours using the paint shaker, and the concentration liquid of moisture powder ink jet recording ink was produced.
HOSUTA palm Pink E (pigment Hoechst A.G. make) The 19.4 sections JON krill 62 The 14.7 sections (34.0% Johnson polymer company make of styrene acrylic copolymer solid content)
Compound (f) The 7.4 sections Ion exchange water The above-mentioned concentration liquid and the following were mixed by 60.3 ******, and the diethylene-glycol monobutyl ether was adjusted to suitableness in addition the viscosity of 2.5cps (25 degrees C), and surface tension 40 dyn/cm. Behind, 1.0-micrometer membrane filter was used and filtered, it filtered using 0.45 more micrometer membrane filter, and moisture powder ink jet recording ink was produced.
The above-mentioned concentration liquid The 12.5 sections Emma Polly TYN-40 The 5.5 sections Glycerol The 10.0 sections Ion exchange water The 72.0 sections [0052] [Example 10] According to the example 9, moisture powder ink jet recording ink was produced using the compound (h).
[0053] [Example 11] The following raw material was mixed, it distributed for 24 hours using the paint shaker, and the concentration liquid of moisture powder ink jet recording ink was produced.
HANZA brilliant yellow 5GX02 (pigment: Hoechst A.G. make) The 19.0 sections JON krill 62 The 8.8 sections Emulgen A-90 The 4.6 sections Compound (e) The 4.8 sections Ion exchange water The 64.2 section above-mentioned concentration liquid and the following were mixed, and the diethylene-glycol monobutyl ether was adjusted to suitableness in addition the viscosity of 2.5cps (25 degrees C), and surface tension 40 dyn/cm. Behind, 1.0-micrometer membrane filter was used and filtered, it filtered using 0.45 more micrometer membrane filter, and moisture powder ink jet recording ink was produced.
The above-mentioned concentration liquid The 12.5 sections Emma Polly TYN-40 The 5.5 sections Glycerol The 10.0 sections Ion exchange water The 72.0 sections [0054] [Example 12] According to the example 11, moisture powder ink jet recording ink was produced using the compound (j).
[0055] [Example 13] The following raw material was mixed, it distributed for 24 hours using the paint shaker, and the concentration liquid of moisture powder ink jet recording ink was produced.
IRUGA gin yellow 2GLTE (pigment: Ciba-Geigy make) The 19.0 sections JON krill 62 The 8.8 sections Emulgen A-90 The 7.0 sections Compound (k) The 8.0 sections Ion exchange water The above-mentioned concentration liquid and the following were mixed by 64.2 ******, and the diethylene-glycol monobutyl ether was adjusted to suitableness in addition the viscosity of 2.5cps (25 degrees C), and surface tension 40 dyn/cm. Behind, 1.0-micrometer membrane filter was used and filtered, it filtered using 0.45 more micrometer membrane filter, and moisture powder ink jet recording ink was produced.
The above-mentioned concentration liquid The 12.5 sections Emma Polly TYN-40 The 5.5 sections Glycerol The 10.0 sections Ion exchange water The 72.0 sections [0056] [Example 14] According to the example 13, moisture powder ink jet recording ink was produced using the compound (l).
[0057] [Example 15] The following raw material was mixed, it distributed for 24 hours using the paint

shaker, and the concentration liquid of moisture powder ink jet recording ink was produced. HOSUTA palm violet RL special (pigment: Hoechst A.G. make) The 14.5 sections JON krill 61J The 16.1 sections Emulgen A-90 The 5.0 sections Compound (g) The 3.6 sections Ion exchange water The above-mentioned concentration liquid and the following were mixed by 62.9 ******, and the diethylene-glycol monobutyl ether was adjusted to suitableness in addition the viscosity of 2.5cps (25 degrees C), and surface tension 40 dyn/cm. Behind, 1.0-micrometer membrane filter was used and filtered, it filtered using 0.45 more micrometer membrane filter, and moisture powder ink jet recording ink was produced.

The above-mentioned concentration liquid The 15.0 sections Emma Polly TYN-40 The 5.5 sections Glycerol The 10.0 sections Ion exchange water The 69.5 sections [0058] [Example 16] According to the example 15, moisture powder ink jet recording ink was produced using the compound (m).

[0059] [Example 17] The following raw material was mixed, it distributed for 24 hours using the paint shaker, and the concentration liquid of moisture powder ink jet recording ink was produced.

MONAKU 800 (pigment: Cabot Corp. make) The 14.5 sections JON krill 61J The 16.1 sections Emulgen A-90 The 5.0 sections Pigment agent a The 6.0 sections Ion exchange water The above-mentioned concentration liquid and the following were mixed by 62.9 ******, and the diethylene-glycol monobutyl ether was adjusted to suitableness in addition the viscosity of 2.5cps (25 degrees C), and surface tension 40 dyn/cm. Behind, 1.0-micrometer membrane filter was used and filtered, it filtered using 0.45 more micrometer membrane filter, and moisture powder ink jet recording ink was produced.

The above-mentioned concentration liquid The 15.0 sections Emma Polly TYN-40 The 5.5 sections Glycerol The 10.0 sections Ion exchange water The 69.5 sections [0060] [Example 18] According to the example 17, moisture powder ink jet recording ink was produced using a compound (j) and (n).

[0061] [Example 1 of a comparison] The following raw material was mixed, it distributed for 12 hours using the paint shaker, and the concentration liquid of moisture powder ink jet recording ink was produced.

RIONORU blue FG-7330 The 0.0 sections JON krill 61J The 16.4 sections Emulgen A-90 The 5.0 sections Ion exchange water The 58.6 section above-mentioned concentration liquid and the following were mixed, and the diethylene-glycol monobutyl ether was adjusted to suitableness in addition the viscosity of 2.5cps (25 degrees C), and surface tension 40 dyn/cm. Behind, 1.0-micrometer membrane filter was used and filtered, it filtered using 0.45 more micrometer membrane filter, and moisture powder ink jet recording ink was produced.

The above-mentioned concentration liquid The 12.5 sections Emma Polly TYN-40 The 5.5 sections Glycerol The 10.0 sections Ion exchange water The 72.0 sections [0062] [Example 2 of a comparison] The following raw material was mixed, it distributed for 24 hours using the paint shaker, and the concentration liquid of moisture powder ink jet recording ink was produced.

HOSUTA palm Pink E The 20.0 sections JON krill 62 The 14.7 sections Emulgen A-90 The 5.0 sections Ion exchange water The 60.3 section above-mentioned concentration liquid and the following were mixed, and the diethylene-glycol monobutyl ether was adjusted to suitableness in addition the viscosity of 2.5cps (25 degrees C), and surface tension 40 dyn/cm. Behind, 1.0-micrometer membrane filter was used and filtered, it filtered using 0.45 more micrometer membrane filter, and moisture powder ink jet recording ink was produced.

The above-mentioned concentration liquid The 12.5 sections Emma Polly TYN-40 The 5.5 sections (made in 44.8% Gifu shellac factory of styrene acrylic copolymer solid content)

Glycerol The 10.0 sections Ion exchange water The 72.0 sections [0063] [Example 3 of a comparison] The following raw material was mixed, it distributed for 24 hours using the paint shaker, and the concentration liquid of moisture powder ink jet recording ink was produced.

HANZA brilliant yellow 5GX02 The 20.0 sections JON krill 62 The 8.8 sections Emulgen A-90 The 7.0 sections Ion exchange water The 64.2 section above-mentioned concentration liquid and the following were mixed, and the diethylene-glycol monobutyl ether was adjusted to suitableness in addition the viscosity of 2.5cps (25 degrees C), and surface tension 40 dyn/cm. Behind, 1.0-micrometer membrane filter was used and filtered, it filtered using 0.45 more micrometer membrane filter, and moisture

powder ink jet recording ink was produced.

The above-mentioned concentration liquid The 12.5 sections Emma Polly TYN-40 The 5.5 sections Glycerol The 10.0 sections Ion exchange water The 72.0 sections [0064] [Example 4 of a comparison] The following raw material was mixed, it distributed for 24 hours using the paint shaker, and the concentration liquid of moisture powder ink jet recording ink was produced.

IRUGA gin yellow 2GLTE The 20.0 sections JON krill 62 The 8.8 sections Emulgen A-90 The 7.0 sections Ion exchange water The 64.2 section above-mentioned concentration liquid and the following were mixed, and the diethylene-glycol monobutyl ether was adjusted to suitableness in addition the viscosity of 2.5cps (25 degrees C), and surface tension 40 dyn/cm. Behind, 1.0-micrometer membrane filter was used and filtered, it filtered using 0.45 more micrometer membrane filter, and moisture powder ink jet recording ink was produced.

The above-mentioned concentration liquid The 15.0 sections Emma Polly TYN-40 The 5.5 sections Glycerol The 10.0 sections Ion exchange water The 69.5 sections [0065] [Example 5 of a comparison] The following raw material was mixed, it distributed for 24 hours using the paint shaker, and the concentration liquid of moisture powder ink jet recording ink was produced.

A HOSUTA palm violet RL special The 16.0 sections JON krill 61J The 16.1 sections Emulgen A-90 The 5.0 sections Ion exchange water The 62.9 section above-mentioned concentration liquid and the following were mixed, and the diethylene-glycol monobutyl ether was adjusted to suitableness in addition the viscosity of 2.5cps (25 degrees C), and surface tension 40 dyn/cm. Behind, 1.0-micrometer membrane filter was used and filtered, it filtered using 0.45 more micrometer membrane filter, and moisture powder ink jet recording ink was produced.

The above-mentioned concentration liquid The 15.0 sections Emma Polly TYN-40 The 5.5 sections Glycerol The 10.0 sections Ion exchange water The 69.5 sections [0066] [Example 6 of a comparison] The following raw material was mixed, it distributed for 24 hours using the paint shaker, and the concentration liquid of moisture powder ink jet recording ink was produced.

MONAKU 800 The 16.0 sections JON krill 61J The 16.1 sections Emulgen A-90 The 5.0 sections Ion exchange water The 62.9 section above-mentioned concentration liquid and the following were mixed, and the diethylene-glycol monobutyl ether was adjusted to suitableness in addition the viscosity of 2.5cps (25 degrees C), and surface tension 40 dyn/cm. Behind, 1.0-micrometer membrane filter was used and filtered, it filtered using 0.45 more micrometer membrane filter, and moisture powder ink jet recording ink was produced.

The above-mentioned concentration liquid The 15.0 sections Emma Polly TYN-40 The 5.5 sections Glycerol The 10.0 sections Ion exchange water The 69.5 sections [0067] While investigating the existence of sedimentation of a pigment, and viscosity change as preservation stability of the moisture powder ink jet recording ink produced according to examples 1-19 and the examples 1-6 of a comparison, it printed by having filled up the cartridge of Epson HG5130, and blinding nature was tested.

[0068] After leaving 30 cc of <preservation stability> recording ink for one month at 60 degrees C for a screw-cap bottle (Nichiden-Rika Glass Co., Ltd.), while investigating the existence of sedimentation of a pigment, the viscosity in 25 degrees C was measured by the Brookfield viscometer (Tokyo Keiki Co., Ltd.).

With no sedimentation of a pigment O Those of a pigment with sedimentation x [0069] <Viscosity> With no viscosity change O It thickens slightly. ** thickening x [0070] Printing was performed for <blinding nature> continuation 1 hour, and the existence of blinding generating was investigated.

With no blinding generating O It is blinding generating at 30 minutes after printing initiation and from 15 minutes after blinding generating ** printing initiation and within 15 minutes. x [0071]

[Table 2]

記録液の種類	目詰まり性		顔料の沈降有無	粘度変化
	初期	1ヶ月後	1ヶ月後	1ヶ月後
実施例1	○	○	○	○
実施例2	○	○	○	○
実施例3	○	○	○	○
実施例4	○	○	○	○
実施例5	○	○	○	○
実施例6	○	○	○	○
比較例1	△	×	△	×
実施例7	○	○	○	○
実施例8	○	○	○	○
実施例9	○	○	○	○
実施例10	○	○	○	○
比較例2	×	×	×	×
実施例11	○	○	○	○
実施例12	○	○	○	○
比較例3	△	×	×	×
実施例13	○	○	○	○
実施例14	○	○	○	○
比較例4	×	×	×	×
実施例15	○	○	○	○
実施例16	○	○	○	○
比較例5	×	×	×	×
実施例17	○	○	○	○
実施例18	○	○	○	○
実施例19	○	×	△	×
比較例6	△	×	△	○

[0072]

[Effect of the Invention]

[Effect of the Invention] The recording ink which gives a waterproof good record object by this invention while carrying out through water came to be obtained. Thereby, constraint of the recorded body decreased very much and the expansion to the application of the aquosity recording ink which producing waterproof lack under the effect of the conventional recorded body had was attained.

[Translation done.]